

Europäisches Patentamt
European Patent Office
Office européen des brevets



1 Publication number:

0 604 798 Å1

12

# **EUROPEAN PATENT APPLICATION**

(2) Application number: 93119754.5

2 Date of filing: 08.12.93

(a) Int. CI.5. **A01N 37/28**, A01N 37/52, A01N 43/40, A01N 43/58, C07C 257/22

Priority: 29.12.92 US 998105
 29.12.92 US 998104
 29.12.92 US 998101

① Date of publication of application: 06.07.94 Bulletin 94/27

Designated Contracting States:
AT BE CH DE DK ES FR GB GR IE IT LI LU NL
PT SE

Applicant: AMERICAN CYANAMID COMPANY One Cyanamid Plaza Wayne New Jersey 07470(US)

Inventor: Furch, Joseph Augustus
68 Northbrook Avenue
Lawrenceville, New Jersey(US)
Inventor: Kuhn, David George
2 Adrian Place
Newton, Pennsylvania(US)
Inventor: Hunt, David Allen
9 Water Lily Way
Newton, Pennsylvania(US)
Inventor: Lew, Albert Chieh
7 Cambridge Way

Princeton Junction, New Jersey 08850(US) Inventor: Gronostajski, Cynthia Emma 530 Roebling Avenue Trenton, New Jersey 08611(US)

Representative: Wächtershäuser, Günter, Dr. Tal 29
D-80331 München (DE)

N-arylhydrazine derivatives as insecticidal and acaricidal agents.

(5) There are provided N-arylhydrazine derivatives of formula I

(I)

the use thereof for the control of insect and acarid pests and methods and compositions for the protection of crops from the damage and loss caused by said pests.

## **BACKGROUND OF THE INVENTION**

Certain insect and acarid pests are harmful and cause enormous losses annually in agricultural crops, stored products and human and animal health. It is an object of this invention to provide substituted Narylhydrazine derivatives which are effective agents for the control of pestiferous insects and acarina.

It is another object of this invention to provide a method for the protection of important agronomic crops from the harmful and damaging effects caused by insect and acarid pests.

It is a further object of this invention to provide insecticidal and acaricidal compositions.

# SUMMARY OF THE INVENTION

The present invention provides a method for the control of insects or acarina which comprises contacting said insects or acarina or their food supply, breeding ground or habitat with an insecticidally effective amount of an N-arylhydrazine derivative of formula I

(I)

n

Q

10

15

20

25

35

40

is C-R4 or N;

is C-R<sub>5</sub> or N;

is C-R $_6$  or N with the proviso that one of A, B or W must be other than N; is hydrogen, halogen, CN, NO2,  $C_1$ - $C_6$  alkyl,  $C_1$ - $C_6$  haloalkyl,  $C_1$ - $C_6$  alkoxy or C<sub>1</sub>-C<sub>6</sub> haloalkoxy;

is an integer of O, 1 or 2;

is

$$N = \langle {}_{R}^{NR_{3}R_{16}}, N = \langle {}_{R}^{X_{1}}, {}_{N}^{R_{2}} \rangle \rangle$$

R

45

50

55

is hydrogen, C1-C10 alkyl optionally substituted with one or more halogens, C3- $C_6 \quad \text{cycloalkyl}, \quad C_1 - C_4 \text{ alkoxy}, \quad C_1 - C_4 \text{ haloalkoxy}, \\ (C_1 - C_4 \text{ alkyl}) \\ SO_x, \quad (C_1 - C_4 \text{ haloalkyl}) \\ S$ kyl)SOx, phenyl optionally substituted with one to three halogen, C1-C4 alkyl,  $C_1$ - $C_4$  haloalkyl,  $C_1$ - $C_4$  alkoxy,  $C_1$ - $C_4$  haloalkoxy,  $(C_1$ - $C_4$  alkyl)SO<sub>x</sub>,  $(C_1$ - $C_4$  haloalkyl)SOx, NO2 or CN groups, or phenoxy optionally substituted with one to three halogen, C1-C4 alkyl, C1-

 $C_4 \ haloalkyl, \ C_1-C_4 \ alkoxy, \ C_1-C_4 \ haloalkoxy, \ (C_1-C_4 \ alkyl) SO_x, \ (C_1-C_4 \ haloalkyl)-C_4 \ haloalkyl, \ C_1-C_4 \ haloalkyl, \ C_1-C$ SOx, NO2 or CN groups,

C<sub>3</sub>-C<sub>12</sub> cycloalkyl optionally substituted with one or more halogens, C<sub>1</sub>- $C_6\,alkyl,\;C_1-C_6\,haloalkyl,\;C_1-C_4\,alkoxy,\;C_1-C_4\,haloalkoxy,\;(C_1-C_4\,alkyl)SO_x,\;(C_1$ C4 haloalkyl)SOx, phenyl optionally substituted with one to three halogen, C1- $C_4$  alkyl,  $C_1$ - $C_4$  haloalkyl,  $C_1$ - $C_4$  alkoxy,  $C_1$ - $C_4$  haloalkoxy,  $NO_2$  or CN groups, or phenoxy optionally substituted with one to three halogen, C1-C4 alkyl, C1-C<sub>4</sub> haloalkyl, C<sub>1</sub>-C<sub>4</sub> alkoxy, C<sub>1</sub>-C<sub>4</sub> haloalkoxy, NO<sub>2</sub> or CN groups, or

phenyl optionally substituted with one or more halogen, C1-C4 alkyl, C1- $C_4$  haloalkyl,  $C_1$ - $C_4$  alkoxy,  $C_1$ - $C_4$  haloalkoxy,  $NO_2$  or CN groups; are each independently hydrogen or C1-C4 alkyl;

R<sub>1</sub> and R<sub>2</sub>

#### EP 0 604 798 A1

R<sub>3</sub> and R<sub>16</sub>

5

10

15

20

25

30

35

40

45

50

55

R<sub>3</sub> and R<sub>16</sub>

R<sub>4</sub>, R<sub>5</sub> and R<sub>6</sub>

R<sub>7</sub>, R<sub>8</sub> and R<sub>9</sub>

Rio

are each independently hydrogen,

 $C_1\text{-}C_1\text{-}\text{o}$ alkyl optionally substituted with one or more halogen, hydroxy,  $C_1\text{-}C_4$  alkoxy,  $(C_1\text{-}C_4$  alkyl)SO<sub>x</sub>, CONR<sub>7</sub> R<sub>8</sub>, CO<sub>2</sub> R<sub>9</sub>, R<sub>10</sub>, R<sub>11</sub>, C<sub>3</sub>-C<sub>6</sub> cycloalkyl optionally substituted with one to three halogen, C<sub>1</sub>-C<sub>4</sub> alkyl, C<sub>1</sub>-C<sub>4</sub> haloalkyl, C<sub>1</sub>-C<sub>4</sub> alkoxy, C<sub>1</sub>-C<sub>4</sub> haloalkoxy, NO<sub>2</sub> or CN groups,

phenyl optionally substituted with one or more halogen,  $C_1$ - $C_4$ alkyl,  $C_1$ - $C_4$ haloalkyl,  $C_1$ - $C_4$ alkoxy,  $C_1$ - $C_4$ haloalkoxy,  $C_2$  or CN groups, or pyridyl optionally substituted with one or more halogen,  $C_1$ - $C_4$ alkyl,  $C_1$ - $C_4$ haloalkoxy,  $C_1$ - $C_4$ alkoxy,  $C_1$ - $C_4$ haloalkoxy,  $C_2$  or CN groups,

 $C_3$ - $C_{10}$  alkenyl optionally substituted with one or more halogen, hydroxy,  $C_1$ - $C_4$  alkoxy,  $(C_1$ - $C_4$  alkyl)SO<sub>x</sub>, CONR<sub>7</sub>R<sub>8</sub>, CO<sub>2</sub>R<sub>9</sub>, R<sub>10</sub>, R<sub>11</sub>, C<sub>3</sub>-C<sub>6</sub> cycloalkyl optionally substituted with one to three halogen, C<sub>1</sub>-C<sub>4</sub> alkyl, C<sub>1</sub>-C<sub>4</sub> haloalkyl, C<sub>1</sub>-C<sub>4</sub> alkoxy, C<sub>1</sub>-C<sub>4</sub> haloalkoxy,NO<sub>2</sub> or CN groups,

phenyl optionally substituted with one or more halogen,  $C_1$ - $C_4$ alkyl,  $C_1$ - $C_4$ haloalkyl,  $C_1$ - $C_4$ alkoxy,  $C_1$ - $C_4$ haloalkoxy,  $C_2$  or CN groups, or pyridyl optionally substituted with one or more halogen,  $C_1$ - $C_4$ alkyl,  $C_1$ - $C_4$ haloalkoxy,  $C_1$ - $C_4$ 

 $C_3$ - $C_{10}$ alkynyl optionally substituted with one or more halogen, hydroxy,  $C_1$ - $C_4$ alkoxy,  $(C_1$ - $C_4$ alkyl)SO<sub>x</sub>, CONR<sub>7</sub>R<sub>8</sub>, CO<sub>2</sub>R<sub>9</sub>, R<sub>10</sub>, R<sub>11</sub>, C<sub>3</sub>-C<sub>6</sub>cycloalkyl optionally substituted with one to three halogen, C<sub>1</sub>-C<sub>4</sub>alkyl, C<sub>1</sub>-C<sub>4</sub> haloalkoxy,NO<sub>2</sub> or CN groups, phenyl optionally substituted with a second control of the co

phenyl optionally substituted with one or more halogen,  $C_1$ - $C_4$ alkyl,  $C_1$ - $C_4$ haloalkyl,  $C_1$ - $C_4$ alkoxy,  $C_1$ - $C_4$ haloalkoxy,  $C_2$  or  $C_1$  groups, or pyridyl optionally substituted with one or more halogen,  $C_1$ - $C_4$ alkyl,  $C_1$ - $C_4$ haloalkoxy,  $C_1$ - $C_4$ haloalkoxy,  $C_1$ - $C_4$  alkoxy,  $C_1$ - $C_4$ haloalkoxy,  $C_2$  or  $C_1$ 0 groups,

 $C_3\text{-}C_{12}\text{cycloalkyl}$  optionally substituted with one or more halogen, hydroxy,  $C_1\text{-}C_4$  alkoxy,  $(C_1\text{-}C_4$  alkyl)SO\_x, CONR\_7R\_8, CO\_2R\_9, R\_{10}, R\_{11}, C\_3\text{-}C\_6\text{cycloalkyl} optionally substituted with one to three halogen,  $C_1\text{-}C_4$  alkyl,  $C_1\text{-}C_4$  haloalkyl,  $C_1\text{-}C_4$  haloalkoxy, NO\_2 or CN groups, phenyl optionally substituted with one or more halogen,  $C_1\text{-}C_4$  alkyl,  $C_1\text{-}C_4$  haloalkoxy,  $C_1\text{-}C_4$  haloalkoxy,  $C_1\text{-}C_4$  haloalkoxy,  $C_1\text{-}C_4$  haloalkoxy,  $C_1\text{-}C_4$  haloalkoxy,  $C_1\text{-}C_4$  haloalkyl,  $C_1\text{-}C_4$  haloalkyl,  $C_1\text{-}C_4$  haloalkoxy, NO\_2 or CN groups, or pyridyl optionally substituted with one or more halogen,  $C_1\text{-}C_4$  alkyl,  $C_1\text{-}C_4$  haloalkyl,  $C_1\text{-}C_4$  alkoxy,  $C_1\text{-}C_4$  haloalkoxy, NO\_2 or CN groups or may be taken together to form a ring represented by the structure

(CH<sub>2</sub>)<sub>p</sub>X<sub>r</sub>

3

are each independently hydrogen, halogen, CN, NO<sub>2</sub>, (C<sub>1</sub>-C<sub>4</sub> alkyl)SO<sub>x</sub>, (C<sub>1</sub>-C<sub>4</sub> haloalkyl)SO<sub>x</sub>, C<sub>1</sub>-C<sub>6</sub> haloalkyl, C<sub>1</sub>-C<sub>6</sub> haloalkyl, C<sub>1</sub>-C<sub>6</sub> alkoxy or C<sub>1</sub>-C<sub>6</sub> haloalkoxy; are each independently hydrogen or C<sub>1</sub>-C<sub>4</sub> alkyl; is NR<sub>12</sub>R<sub>13</sub>,

 $(CH_2)_p$   $X_r$  or CH  $(CH_2)_p$   $(CH_2)_p$ 

R<sub>11</sub>

is

 $R_{12},\,R_{13},\,R_{14}$  and  $R_{15}$ 

are each independently hydrogen or C1-C4 alkyl;

 $X_1$ 

is chlorine, bromine, or fluorine;

Χ

is O, S or NR<sub>14</sub>;

r

is an integer of 0 or 1;

p and m

are each independently an integer of 0, 1, 2 or 3 with the provisos that only one of p, m or r can be 0 and that the sum of p + m + r must be 4, 5 or 6;

is an integer of 0, 1 or 2; or

the acid addition salts thereof, with the proviso that when Q is

20

5

10

15

$$N = <_{R}^{X_1}$$

R is  $C_1$ - $C_5$  alkyl and  $X_1$  is chlorine, then either at least one of A, B or W must be N or  $R_4$ ,  $R_5$ ,  $R_6$  and Y must be other than hydrogen and n must be O and with the further proviso that when

Q is

30

25

$$=$$

R is phenyl or substituted phenyl and X<sub>1</sub> chlorine, then at least one of A, B or W must be N.

The present invention further provides N-arylamidrazone compounds of formula I wherein A, B, W, Y, n, and R<sub>1</sub>, are as described hereinabove and Q is

$$N = \langle NR_3R_{16} \rangle$$

40

45

50

55

with the proviso that when all of A, B and W are other than N, then R and one of  $R_3$  or  $R_{16}$  must be other than hydrogen and with the further proviso that when one of A, B or W is N, then Y,  $R_4$ ,  $R_5$  or  $R_6$  must be other than  $C_1$ - $C_{10}$ alkyl.

Compositions and methods for the protection of growing plants from attack and infestation by insects and acarina are also provided.

## DETAILED DESCRIPTION OF THE INVENTION

A variety of insects and acarina cause great economic loss by damaging or destroying agricultural crops and other valuable plants; by aiding in the spread and development of bacteria, fungi and viruses that produce diseases of plants; and by destroying or lowering the value of stored foods, other products and possessions. Insects and acarina present some of the farmers' greatest problems the world over. The need for alternative and effective insect and acarid control is a global concern.

It has now been found that the substituted N-arylhydrazone derivatives of formula I are especially efficacious insecticidal and acaricidal agents, particularly against Coleoptera, Lepidoptera and Acarina.

The formula la amidrazone compounds of the present invention have the structural formula

$$\begin{array}{c|c}
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& &$$

wherein A, B, W, Y, n, R, R<sub>1</sub>, R<sub>3</sub> and R<sub>16</sub> are described hereinabove. The term halogen as used in the specification and claims designates chlorine, fluorine, bromine or iodine. The term acid addition salts designates those salts formed by acids commonly known in the art such as hydrogen chloride, hydrogen bromide, hydrogen bisulfate, hemi-hydrogen sulfate and the like. In the above definition when n is O then Y is hydrogen.

Preferred compounds of the invention are those wherein R,  $R_3$  and  $R_{16}$  are each independently hydrogen or  $C_1$ - $C_6$  alkyl, A is C- $R_4$ , B is C- $R_5$ , W is C- $R_6$ , Y is halogen and n is 1. Particularly preferred compounds are those wherein  $R_1$  is hydrogen,  $R_4$  is halogen,  $R_5$  is hydrogen and/or  $R_6$  is  $C_1$ - $C_6$  alkyl substituted with one or more halogens, preferably trifluoromethyl.

Other preferred compounds of the invention are compounds having the structure

$$R_6 \xrightarrow{\begin{array}{c} Y \\ R_1 \\ N \end{array}} NR_3R_{16}$$

wherein

5

20

25

30

35

40

R is C<sub>1</sub>-C<sub>10</sub>alkyl;

R<sub>1</sub> is hydrogen or C<sub>1</sub>-C<sub>4</sub> alkyl;

 $R_3$  is  $C_1$ - $C_{10}$  alkyl;

R<sub>16</sub> is hydrogen or C<sub>1</sub>-C<sub>10</sub> alkyl; and

R<sub>4</sub>, R<sub>6</sub> and Y are each independently hydrogen, halogen, CN, NO<sub>2</sub>, C<sub>1</sub>-C<sub>6</sub> alkyl, C<sub>1</sub>-C<sub>6</sub> haloalkyl, C<sub>1</sub>-C<sub>1</sub> alkeys, or C<sub>1</sub>-C<sub>2</sub> haloalkyl, C<sub>1</sub>-C

 $C_6$  alkoxy, or  $C_1$ - $C_6$  haloalkoxy.

The N-arylamidrazones of formula Ia may be prepared by reacting an acid chloride, hydrazone (hydrazinoyl chloride) of formula II with an amine compound, HNR<sub>3</sub>R<sub>16</sub>, as shown in flow diagram I.

#### Flow Diagram I

Compounds of formula II may be prepared by reacting a suitable arylhydrazine of formula III with the appropriate acid chloride, RCOCI, to obtain an N-arylhydrazide of formula IV and reacting the formula IV hydrazide with a halogenating agent such as thionyl halide to give the desired formula II N-arylhydrazinoyl halide product. The reaction is illustrated in flow diagram II.

#### Flow Diagram II

The substituted N-arylhydrazine derivatives of the present invention are effective for controlling insect and acarid pests. Said compounds are also effective for protecting growing or harvested crops from attack and infestation by such pests.

Compounds useful in the inventive method include N-arylhydrazinoyl halide compounds of formula II. The insecticidal and acaricidal formula II hydrazinoyl halides of the present invention have the structural formula

wherein A, B, W, Y, n, R,  $R_1$  and  $X_1$  are described hereinabove.

10

15

20

25

35

40

50

55

Preferred compounds of formula II are those compounds wherein  $R_1$  is hydrogen, A is C-R<sub>4</sub>, B is C-R<sub>5</sub>, W is C-R<sub>6</sub>, Y is halogen or nitro and n is 1. Particularly preferred are those wherein  $R_4$  is halogen,  $R_5$  is hydrogen and  $R_6$  is  $C_1$ -C<sub>6</sub> alkyl substituted with one or more halogens, preferably trifluoromethyl.

Other preferred compounds of formula II are those in which R is optionally substituted  $C_3$ - $C_{12}$  cycloalkyl or  $C_1$ - $C_{10}$  haloalkyl, preferably  $C_1$ - $C_6$  haloalkyl.

Compounds of formula II wherein  $X_1$  is fluorine may be prepared from compounds of formula II wherein  $X_1$  is chlorine or bromine by a halogen exchange reaction using sodium fluoride or hydrogen fluoride such as that described by March in Advanced Organic Chemistry, 4 Ed. (1992), p. 438.

Further compounds useful in the method of invention include substituted carboxylic acid, N-aryl-hydrazide compounds of formula V.

The insecticidal and acaricidal formula V N-arylhydrazides of the present invention have the structural formula

10 '

Preferred compounds of formula V for use in the method of the invention are those compounds wherein R is hydrogen or  $C_1$ - $C_6$ alkyl, A is C- $R_4$ , B is C- $R_5$ , W is C- $R_6$ , Y is halogen or nitro and n is 1. Particularly preferred formula V N-arylhydrazides are those wherein  $R_4$  is halogen,  $R_5$  is hydrogen and  $R_6$  is  $C_1$ - $C_6$ alkyl substituted with one or more halogens, preferably trifluoromethyl.

Compounds of formula V may be prepared by reacting a suitable arylhydrazine of formula VI with the appropriate acid chloride, RCOCI, to yield the desired N-arylhydrazide of formula V. The reaction is illustrated in flow diagram III.

## Flow Diagram III

20

25

30

35

Growing or harvested crops may be protected from attack or infestation by insect or acarid pests by applying to the foliage of the crops, or to the soil or water in which they are growing, a pesticidally effective amount of a formula | N-arylhydrazine derivative.

In practice, generally about 10 ppm to 10,000 ppm, preferably about 100 to 5,000 ppm of the formula I compound dispersed in a liquid carrier, when applied to the plants or the soil or water in which they are growing, is effective to protect the plants from insect and acarina attack and infestation. Soil application of the formula I compounds is particularly effective for the control of the post-embryonic development stages of Coleoptera and Diptera. Applications, such as spray applications, of compositions of the invention are generally effective at rates which provide about 0.125 kg/ha to about 250 kg/ha, preferably about 10 kg/ha to 100 kg/ha. Of course, it is contemplated that higher or lower rates of application of the N-arylhydrazine derivatives may be used dependent upon the prevailing environmental circumstances such as population density, degree of infestation, stage of plant growth, soil conditions, weather conditions and the like.

Advantageously, the formula I compounds may be used in conjunction with, or in combination with other biological and chemical control agents including other insecticides, nematicides, acaricides, molluscicides, fungicides and bactericides such as nuclear polyhedrosis viruses, pyrroles, halobenzoylureas, pyrethroids, carbamates, phosphates, and the like.

Typical formulations suitable for the formula I N-arylhydrazine derivatives are granular compositions, flowable compositions, wettable powders, dusts, microemulsions, emulsifiable concentrates and the like. All compositions which lend themselves to soil, water and foliage application and provide effective plant protection are suitable. Compositions of the invention include the formula I N-arylhydrazine derivatives admixed with an inert solid or liquid carrier.

Where compositions of the invention are to be employed in combination treatments with other biological or chemical agents, the composition may be applied as an admixture of the components or may be applied sequentially.

For a more clear understanding of the invention, specific examples thereof are set forth below. These examples are merely illustrative, and are not to be understood as limiting the scope and underlying principles of the invention in any way.

#### **EXAMPLE 1**

5

10

25

30

40

45

50

55

## Preparation of 2,2-Dimethylpropionic acid,2-(2,6-dichloro- $\alpha$ , $\alpha$ , $\alpha$ -trifluoro-p-tolyl)hydrazid

 $F_3C \longrightarrow CF_3 \longrightarrow CF_3 \longrightarrow NHNH$ 

A solution of 2,6-dichloro-4-(trifluoromethyl)phenylhydrazine (50.0 g, 0.20 mol) in methylene chloride is treated dropwise with trimethylacetyl chloride (30.6 g, 0.254 mol), stirred for 30 minutes, treated with 10% aqueous NaOH and stirred for 3 hours. The phases are separated; the organic phase is washed with water, dried over MgSO<sub>4</sub> and concentrated in vacuo to give an off-white solid residue. The solid is recrystallized from 1,2-dichloroethane to give the title product as a white solid, 55 g (82% yield), mp 140-141°, identified by ¹HNMR, ¹3CNMR and IR spectral analyses.

#### **EXAMPLES 2-42**

#### Preparation of substituted N-arylhydrazide derivatives

Using essentially the same procedure described above for Example 1 and substituting the appropriate arylhydrazine and acid chloride, the compounds shown in Table I are prepared and identified by <sup>1</sup>HNMR, <sup>13</sup>NMR and IR spectral analyses.

# EP 0 604 798 A1

# TABLE I

Yn	0
	- 11
и / / />— инин	
~ _ / //////	· K
Ά <u> </u>	

	Example Number	_ <u>A</u> _	В	ш	Yn	R	mp °C
10	2	C-C1	СН	C-CF <sub>3</sub>	6-C1	(CH <sup>3</sup> ) <sup>5</sup> CHCH <sup>5</sup>	135-136
15	3	C-C1	СН	C-C1	6-C1	(CH <sub>3</sub> ) <sub>3</sub> C	124-125.5
	4	C-C1	СН	СН	6-C1	(CH <sub>3</sub> )3C	114-115
20	5	C-Br	СН	C-CF <sub>3</sub>	6-Br	(CH <sub>3</sub> ) <sub>3</sub> C	118-120
25	6	C-Br	СН	C-CF3	6-Br	CH3	173-175
	7	C-Br	CH	C-CF <sub>3</sub>	6-Br	С <sub>6</sub> Н <sub>5</sub>	181-184

NEDOCID- -ED DEDATORAL

5			mp <sup>O</sup> C 103-106	125-127	188-190	158-159	186-188	121-123	136-139	143-145
10			1					2		
15			R (CH <sub>3</sub> ) <sub>3</sub> C	$(CH_3)_3CCH_2$	SH <sub>2</sub> OIO <u>a</u>	$(CH_3)_2$ CH	cyclopropyl	сн <sub>3</sub> сн <sub>2</sub> с(сн <sub>3</sub> ) <sub>2</sub>	$(CH_3)_3^C$	(CH <sub>3</sub> ) <sub>3</sub> C
20	led)	0 <del>-</del>	I							
25	TABLE I (Continued)	, NHNHN	Yn	6-01	6-01	6-C1	6-C1	6-C1	Ħ	<b>.</b>
30	TABLE	n i i i	W C-C1	C-CF3	c-c1	C-CF3	c-c1	C-CF3	· C-CF3	C-CF3
35		•	B CH	CH	CH	CH	СЖ	HO	ĊH	Н
40										
<b>4</b> 5	•		C-CH <sub>3</sub>	C-Cl	C-C1	C-C1	C-C1	0-01	H-O	c-c1
50			Example Number 8	თ	jo	11	12	13	14	15

....

5			mp <sup>O</sup> C 125-127		151-151.5	138-140	137-139	98-100	101-103	188-189
10						~ <del>'</del> \	CH <sub>3</sub> ) <sub>2</sub>			
15			α <b>γ</b>	(CH <sub>3</sub> ) <sub>3</sub> C	СН <sub>3</sub> ) з С	CF 32	си Всіс <sub>е</sub> н <sub>5</sub> ос(сн <sub>3</sub> )	(CH <sub>3</sub> ) <sub>3</sub> C	$A_{\tilde{\mathbf{r}}}$	cyclohexyl
20	ied)	0 —	ţ	<del></del>			•			
25	TABLE I (Continued)	-NHNHN	Yn 6-C1	5,6-dic1	6-01	6-01	6-61	Ħ	6-01	6-01
30	TABLE		W C-CF3	C-CJ	C-CF3	c-c1	C-CF3	СН	c-cF3	C-C]
35			CH CH	C-C1	СН	СН	СН	СН	СН	CH
40			1					_		
45	·		A C-C1	C-C1	z	c-c1	c-c1	C-CF3	C-C1	c-c1
50			Example Number 16	17	18	19	20	21	22	23

EP 0 604 798 A1

5	:		mp <sup>O</sup> C 104-105	131-132	164-165	172-174	132-134	160~162	140-141	
10			20			<u>ر</u>	13)2			(CH <sub>3</sub> ) <sub>2</sub>
. 15			C <sub>6</sub> H <sub>5</sub> C(CH <sub>3</sub> ) <sub>2</sub>	CF3CF2	(сн <sub>3</sub> ) <sub>2</sub> сн	cyclopropyl	сн <sub>3</sub> сн <sub>2</sub> с(сн <sub>3</sub> ) <sub>2</sub>	<b>Q</b>	$(CH_3)_3^C$	сн <sub>3</sub> (сн <sub>2</sub> ) <sub>5</sub> с(сн <sub>3</sub> ) <sub>2</sub>
20	nued)	ο <del>-</del> α					•			
25	TABLE I (Continued	NHNHN-	Yn 6-C1	6-C1	6-C1	6-C1	6-C1	6-C1	6-Br	6-C1
30	TABLE	T B I B	W C-CF <sub>3</sub>	c-c1	C-C1	C-CF3	c-c1	C-CF <sub>3</sub>	C-CF <sub>3</sub>	C-CJ
35			m H	СН	СН	СН	СН	СН	СН	СН
40 .			C-C1	c-c1	. c-c1	C-C]	c-c1	c-c1	C÷Br	c-c1
50	,		Example Number 24	25	5 6	27	28	29	30	ιε

5			mp ос 178-182	121-123	105-107	119-120	174-175	124-125	170-177.5	105-107
10					сн <sub>3</sub> ) <sub>2</sub>	3)2		) 2		clohexyl
15			R (CH <sub>3</sub> ) <sub>3</sub> C	Χ., 	Eclc <sub>6</sub> H <sub>5</sub> C(CH <sub>3</sub> ) <sub>2</sub>	ClCH <sub>2</sub> C(CH <sub>3</sub> ) <sub>2</sub>	2.2	clcH <sub>2</sub> c(cH <sub>3</sub> ) <sub>2</sub>	(CH3)3C	1-methylcyclohexyl
20	inued)	0								
25	TABLE I (Continued)	۲, - NHNH/	Yn H	6-01	6-C1	6-C1	6-C1	6-C1	5-CF3	6-C1
30	TABL	3   B	C-C1	C-CF3	C-CF <sub>3</sub>	C-CF3	C-CF3	C-C1	СН	C-CF3
35			m z	СН	СН	СН	СН	Н	<b>.</b>	Н
40			A Z	c-c1	C-C1	c-c1	01	C-C1	c-c1	c-c1
45			e 1		Ü	O		U	Ċ	ပ်
50 .			Example Number 32	e e	34	ខ	98	37	38	98

				mp °c 158-160	154-157	118-120
·5				158	154	118
					·	
15			*.	(CH <sub>3</sub> ) <sub>3</sub> C	(сн <sub>3</sub> ) <sub>3</sub> с	(CH <sub>3</sub> ) <sub>3</sub> C
25		ontinued)	NHNHN-	Υn H	5,6-diF	6-Br
30		TABLE I (Continued	γ γ γ γ γ γ γ γ γ γ γ γ γ γ γ γ γ γ γ	3		ý
35				B W	C-F C-F	#1
40						r CH
45				CH P	О Н	C-Br
50	·			Example Number 40	4 1	4 2

**EXAMPLE 43** 

# Preparation of 1-chloro-2,2-dimethylpropionaldehyde, 2-(2,6-Dichloro-a,a,a-trifluoro-p-tolyl)hydrazone

$$F_3C \xrightarrow{C1} NHNH \xrightarrow{O} F_3C \xrightarrow{C1} NHN \xrightarrow{C1} C1$$

A mixture of 2,2-dimethyl-2-(2,6-dichloro- $\alpha$ , $\alpha$ , $\alpha$ -trifluoro-p-tolyl)hydrazide propionic acid (50.0 g, 0.152 mol) and thionyl chloride (53.8 g, 0.452 mol) in toluene is heated at reflux temperature for 8 hours, cooled to room temperature and concentrated in vacuo to give an oil residue. The oil is dissolved in hexanes and passed through a silica gel filtercake. The filtercake is washed with several portions of hexanes. The filtrates are combined and concentrated in vacuo to give the title product as a yellow oil, 47.2 g (90% yield), identified by <sup>1</sup>HNMR, <sup>13</sup>CNMR and IR spectral analyses.

#### **EXAMPLES 44-84**

5

10

15

25

30

35

40

45

50

55

#### Preparation of substituted N-arylhydrazinoyl chlorides

Using essentially the same procedure as described above in Example 43 and substituting the appropriate hydrazide substrate, the compounds shown in Table II are prepared and identified by <sup>1</sup>HMR, <sup>13</sup>CNMR and IR spectral analyses.

# EP 0 604 798 A1

5			o dw	44.5-45.5				
10			1					
15			CH <sub>3</sub> ) <sub>2</sub> CHCH <sub>2</sub>	сн <sup>3</sup> ) <sup>3</sup> с	(сн <sup>3</sup> ) <sup>3</sup> с	. (сн <sub>3</sub> ) <sub>3</sub> с	снз	C <sub>6</sub> H <sub>5</sub>
25	TABLE II	C C C C C C C C C C C C C C C C C C C	Yn 6-C1	6-C1	6-C1	6-Br	6-Br	6-Br
30	Ħ	T I B	W C-CF3	c-c1	СН	O Fi	C-CF3	C-CF3
35			CH	СН	СН	СН	СН	СН
40 45			A C-C1	c-c1	C-C1	ra-o	C-Br	C-Br
50 <sub>.</sub>			Example Number 44	45	46	74	4 8	Q.

5		•	So dm		120				•
10			R (CH <sub>3</sub> ) <sub>3</sub> C	(CH <sub>3</sub> ) <sub>3</sub> CCH <sub>2</sub>	pc1c <sub>6</sub> H <sub>5</sub>	(сн <sub>3</sub> ) <sub>2</sub> сн	cyclopropyl	сн <sub>3</sub> сн <sub>2</sub> с(сн <sub>3</sub> ) <sub>2</sub>	э <sup>є</sup> ( <sup>є</sup> нэ)
20	<del>(</del> }		(CH <sub>3</sub>	(CH <sub>3</sub>	pc1c	(CH <sub>3</sub>	cycl	CH <sup>3</sup> C	(CH <sub>3</sub>
25	TABLE II (Continued)	NHN C	X H	6-C1	6-C1	6-C1	6-C1	6-C1	Ħ
30	TABLE		w c-c1	C-CF <sub>3</sub>	C-C1	C-CF3	C-C1	C-CF3	C-CF3
35			B CH	C <b>H</b>	CH	CH	СН	СН	СН
40			A C-CH <sub>3</sub>	c-c1	C-C1	c-c1	c-c1	c-c1	С-Н
<b>4</b> 5			Example Number 50	51	. 25	ເຕ	54	ស	56

# EP 0 604 798 A1

5			O OE						
10		·					<u>.</u> %	(CH <sub>3</sub> ) <sub>2</sub>	
15	•		(CH <sub>3</sub> ) 3 C		сн <sup>3</sup> ) <sup>3</sup> с	(СН <sub>3</sub> ) <sub>3</sub> С	;;	Eclc <sub>e</sub> H <sub>5</sub> Oc(cH <sub>3</sub> ) <sub>2</sub>	(сн <sup>3</sup> ) <sup>3</sup> с
20	led)	ဂ္ ၾ	l		:		J		
25	TABLE II (Continued)	NHN-	Хи Н	6-C1	5,6-dicl	6-C1	6-C1	6-C1	Ħ
3 <b>0</b>	TABLE I	,	C-CF3	C-CF3	c-c1	C-CF3	c-c1	೧-೧೯3	æ
35			B CH	СН	c-c1	СН	СН	НО	CH
40			A C-C1	c-c1	c-c1	z	c-c1	c-c1	C-CF3
45		٠.	as t						
50			Example Number 57	58	50	09	61	. 62	63

18

WIGOUCID- >ED

## EP 0 604 798 A1

5			O QE						
10			ļ		. 2			<b>.</b>	3)2
15	*		R K	cyclohexyl	с <sup>6</sup> н <sup>5</sup> с(сн <sup>3</sup> ) <sup>2</sup>	$c_{F_3}c_{F_2}$	(CH <sub>3</sub> ) <sub>2</sub> CH	cyclopropyl	cH <sub>3</sub> CH <sub>2</sub> C(CH <sub>3</sub> ) <sub>2</sub>
20	ا۔		;		•				٠.
25	TABLE II (Continued)	NHN C1	Yn 6-C1	6-C1	6-C1	6-01	6-61	6-C1	6-C1
30	TABLE	B I B	C - CF3	c-c1	C-CF3	c-c1	c-c1	C-CF3	c-c1
35								•	
			CH CH	C-CH	C-CH	Ë	Ë	E5	ë
40									
45		·	C-C1	c-c1	0-c1	c-c1	c-c1	c-c1	C-C1
50			Example Number 64	9 2	. 99	67	89	69	20

19

.....

### EP 0 604 798 Å1

5		mp <sup>O</sup> C 110-111					82-88	
10				c(cH <sub>3</sub> ) <sub>2</sub>			(CH <sub>3</sub> ) <sub>2</sub>	<sup>1</sup> 3) 2
15		ω Κ	$(CH_3)_3^C$	сн <sub>3</sub> (сн <sub>2</sub> ) <sub>5</sub> с(сн <sub>3</sub> ) <sub>2</sub>	(CH <sub>3</sub> ) <sub>3</sub> C	المارين پي	pclc <sub>6</sub> H <sub>5</sub> c(cH <sub>3</sub> ) <sub>2</sub>	clcH <sub>2</sub> c(cH <sub>3</sub> ) <sub>2</sub>
20	੍ਰੀ 1					,		
25	TABLE II (Continued)  Yn  C1  B=-A	Уn 6-С1	9-Br	6-C1	æ	6-C1	6-C1	6-01
30	TABLE I	C-CF3	C-CF3	c-c1	c-cl	C-CF3	c-cF3	c-cF3
35		1.						
		m H	CH	CH	z	HO	CH	CH
40 45		C-C1	C-Br	C-C]	Z	c-c1	c-c1	C-CJ
50		Example Number 71	72	73	74	75	76	77

20

אופררכיום -כם מספידים

5			mp O <sub>C</sub>						·
10				3) 2		yclohexyl			
15			α <u>Υ</u>	clcH <sub>2</sub> C(CH <sub>3</sub> ) <sub>2</sub>	$(CH_3)_3^C$	1-methylcyclohexyl	(CH <sub>3</sub> ) <sub>3</sub> C	(CH <sub>3</sub> ) <sub>3</sub> C	$(cH_3)_3c$
20	(p	ت							
25	TABLE II (Continued)	A NH N	Yn 6-C1	6-Cl	5-CF3	6-C1	Ħ	ស ៖ ដ	6-Br
30	TABLE		W CCF <sub>3</sub>	C-C1	СН	c-cF3	СН	Н	į. Li
35			ı				C-CF3		
		•	<b>™</b> 5	CH	, HO	СН	Ů	CH	СН
45			A C-C1	C-C1	C-C1	C-C1	HO	Н	C-Br
50			Example Number 78	7.9	80	81	82	83	84

55 EXAMPLE 85

# Preparation of N-Ethyl-2,2-dimethylpropionamide, 2-(2,6-Dichloro-\alpha,\alpha,\alpha-trifluoro-p-tolylhydrazone

 $F_3C \xrightarrow{C1} + H_2NC_2H_5 \longrightarrow F_3C \xrightarrow{C1} NHN \xrightarrow{NHC_2H_5}$ 

A solution of  $(2,6\text{-dichloro-}\alpha,\alpha,\alpha\text{-trifluoro-}p\text{-tolyl})$ hydrazone 1-chloro-2,2-dimethylpropionaldehyde (20.0 g, 0.0575 mol) in tetrahydrofuran is treated dropwise with 70% aqueous ethylamine (28.0 g, 0.144 mol) at room temperature, stirred for 1 hour and concentrated in vacuo to give a semi-solid residue. The semi-solid is dispersed in ether and water. The phases are separated; the organic phase is washed with water, dried over MgSO<sub>4</sub> and concentrated in vacuo to give the title product as a yellow oil, 19.8 g (97% yield), identified by  $^1$ HNMR,  $^1$ 3CNMR and IR spectral analyses.

#### **EXAMPLES** 86-169

5

10

15

35

40

### Preparation of substituted N-arylamidrazones

Using essentially the same procedure described above in Example 85 and substituting the appropriate hydrazinoylchloride and a suitable amine, the compounds shown in Table III are prepared and identified by <sup>1</sup>HNMR, <sup>13</sup>CNMR and IR spectral analyses.

Hydrochloride salts of the invention may be prepared in accordance with the procedure outlined below.

Example 146 - Preparation of N-Ethyl-2,2-dimethylproprionamide,2-(2,6-dichloro-α,α,α-trifluoro-p-tolyl-hydrazone hydrochloride

$$F_3C \xrightarrow{C1} NHN \xrightarrow{NHC_2H_5} HC1 \qquad F_3C \xrightarrow{C1} NHN \xrightarrow{NHC_2H_5} HC1$$

A stirred mixture of N-ethyl-2,2-dimethylpropionamide, 2-(2,6-dichloro- $\alpha$ , $\alpha$ , $\alpha$ -trifluoro-p-tolylhydrazone (0.1 g, 2.8 mmol) and hexane is bubbled through with HCl gas for a 30 minute period. The resultant reaction mixture is filtered to give the title compound as a white solid, 1.13 g, mp 202-202.5°C.

5			٥ ٥ ٩		48-50			
10			R16 H	Ħ	Ħ	æ į	Ħ	E
15 20			R3 PC1C <sub>6</sub> H <sub>5</sub>	cH3cH2cH2	ch3ch2ch2	cH3cH2cH2	cyclopropyl	снзсн2
25	TABLE III	Yn Yn NR3 R16	(СН <sub>3</sub> ) 3 С	(сн <sup>3</sup> ) <sup>3</sup> с	(CH <sub>3</sub> ) <sub>2</sub> CH	(CH <sub>3</sub> ) <sub>3</sub> CCH <sub>2</sub>	(CH <sub>3</sub> ) <sub>2</sub> CH	(cH <sub>3</sub> ) <sub>3</sub> ccH <sub>2</sub>
30		3   B	Yn 6-C1	6-c1	6-C1	6-01	6-01	6-c1
35			C-CF3	c-c1	C-C1	C-CF3	C-C1	c-cF <sub>3</sub> 6-cl
40		·	GH H	CH	СН	CH	CH	CH
45			S C C C	0-01	C-C1	C-C1	ប្រ-ប	c-c1
50			Example <u>Number</u> 86	87	& &	68	06	91

MIGDOOID- ZED

5			. <i>:</i>	mp. <sup>O</sup> C 62-64					
10				R16.	ж	ж	Ħ	Ħ	Ħ
15 20		(pa	9. 14.	CH <sub>3</sub> CH <sub>2</sub>	cF <sub>3</sub> cH <sub>2</sub>	снзсн2	сн <sub>3</sub> сн <sub>2</sub> сн <sub>2</sub>	CeH5CH2	furfuryl
25 30		TABLE III (Continued)	Yn NR3 R16	R (СН <sub>3</sub> ) <sub>2</sub> СН	(сн <sup>3</sup> ) <sup>3</sup> с	(сн <sup>3</sup> ) <sup>3</sup> с	сн <sub>3</sub> ) <sup>3</sup> с	(сн <sup>3</sup> ) <sup>3</sup> с	(CH <sub>3</sub> ) <sub>3</sub> C
35		TAB	,	C-CF <sub>3</sub> 6-C1	c-cF <sub>3</sub> 6-cl	C-CF <sub>3</sub> 6-Br	c-cF <sub>3</sub> 6-Br	C-CF <sub>3</sub> 6-Br	c-cF <sub>3</sub> 6-Br
40				□ 5 □ 5	U HO	CH	CH	CH	CH
45				A C-C1	0-0	C-Br	C-Br	C-Br	C-Br
50	·			xample lumber 92	6	46	ક	96	76

5		O de		131-135	61-63				100-102.5
10		R.16 H	ж	ж	CH <sub>3</sub>	Ħ	##	æ	Ħ
15 20	( <del>[</del> ]	R3 CH <sub>3</sub> CH <sub>2</sub>	cH <sub>3</sub> cH <sub>2</sub>	ĸ	снз	сн <sub>3</sub> сн <sub>2</sub>	ch <sub>3</sub> ch <sub>2</sub> ch <sub>2</sub>	ch <sub>3</sub> ch <sub>2</sub> ch <sub>2</sub>	Ħ
25	TABLE III (Continued)  Y  NR3R16  B=A	CH <sub>3</sub>	C <sub>6</sub> H <sub>5</sub>	(CH <sub>3</sub> ) <sub>3</sub> C	(CH <sub>3</sub> ) <sub>3</sub> C	(сн <sub>3</sub> ) <sub>3</sub> с	(CH <sub>3</sub> ) <sub>3</sub> C	(сн <sub>3</sub> ) <sub>3</sub> с	о <sup>є</sup> (сн <sup>3</sup> )
30 35	TABLE	Yn 6-Br CF	6-Br C	6-C1 (C	6-c1 (0	6-c1 ((	))	6-c1 ((	6-c1 (
40		E CF 3	C-CF3	c-c1	c-c1	c-c1	C-CF3	H5	C-CF3
45		A B CH	C-Br CH	C-Cl CH	c-c1 CH	C-Cl CH	c-cl cH	C-C1 CH	c-c1 CH
50	·	Example Number 98	66	100	101	102	103	104	105

5				၁၀ ထိ။	78-79.5	· .		.67.5-68.5			65-67
10	ŕ			R 16	æ	снз	<b>II</b>	æ	<b>#</b>	12CH2-	æ
15		<u>(a)</u>	o J		снз	сн <sub>3</sub>	cH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub>	(сн <sup>3</sup> ) <sup>3</sup> с	(CH <sub>3</sub> ) <sub>2</sub> CHCH <sub>2</sub>	-CH2CH2CH2CH2-	cH <sub>3</sub> cH <sub>2</sub>
25		TABLE III (Continued)	NHN R R 6	œ	(CH <sub>3</sub> ) <sub>3</sub> C	(сн <sub>3</sub> ) <sub>3</sub> с	(CH <sub>3</sub> ) <sub>3</sub> c	(сн <sup>3</sup> ) <sup>3</sup> с	(CH <sub>3</sub> ) <sub>3</sub> C	(сн <sup>3</sup> ) <sup>3</sup> с	cyclopropyl
35		TABI	1	Ϋ́	9	F <sub>3</sub> 6-C1	F3 6-C1	F3 6-C1	F3 6-C1	F3 6-C1	:1 6-C1
40				<b></b>	CH C-CF <sub>3</sub>	CH C-CF3	CH C-CF3	CH C-CF3	CH C-CF3	CH C-CF3	CH. C-CI
45				A	. •	C-C]	C-C1	C-C1	C-01	C-C1	C-C1
50				Example Number	106	107	108	109	110	111	112

5			O DE						
10			R16	Ħ	H <sub>2</sub> CH <sub>2</sub> -	CH3 CH2	ж	Ħ	
15	<u>ed)</u>		CH <sub>3</sub> CH <sub>2</sub>	(CH <sub>3</sub> ) <sub>2</sub> CH	-ch <sub>2</sub> ch <sub>2</sub> ch <sub>2</sub> -	cH <sub>3</sub> cH <sub>2</sub>	сн <sub>3</sub> сн <sub>2</sub>	CH <sub>3</sub> CH <sub>2</sub>	
25	TABLE III (Continued)	Yn NR3R16	R CH <sub>3</sub> CH <sub>2</sub> C(CH <sub>3</sub> ) <sub>2</sub>	сн <sup>3</sup> ) <sup>3</sup> с	(сн <sub>3</sub> ) <sub>3</sub> с	CH <sub>3</sub> CH <sub>2</sub> C(CH <sub>3</sub> ) <sub>2</sub>	сн <sub>3</sub> ) <sub>3</sub> с	сн <sub>3</sub> сн <sub>2</sub> с(сн <sub>3</sub> ) <sub>2</sub>	
35	TAI	д — В — В — В — В — В — В — В — В — В —	Yn 6-C1	6-Br	×	6-C1	<b>#</b>	6-01	
40			B W C-CF <sub>3</sub>	CH C-CF3	CH C-CF3	CH C-CF3	CH C-CF3	сн с-с1	
45			A C-C1	C-Br	c-c1	c-c1	c-c1	c-c1	
50		·	Example Number 113	114	115	116	117	118	

MICHAIL >ED

5				၁ <sub>၀</sub> d။			86.5-88.5			
10				R16 H	H <sub>2</sub> CH <sub>2</sub> -	ш	Ħ	H2CH2-	ж	æ
20	ued)	NR3 R <u>1</u> 6 R	; ; ; ;	CH <sub>3</sub> CH <sub>2</sub>	-ch <sub>2</sub> ch <sub>2</sub> ch <sub>2</sub> ch <sub>2</sub> -	CH <sub>3</sub> CH <sub>2</sub>	CH <sub>3</sub> CH <sub>2</sub>	-cH2cH2cH2cH2-	cyclohexyl	ceHscHzcHz
25	TABLE III (Continued)	Y NR	, ·	C6H5C(CH3)2	(сн <sub>3</sub> ) 3 с	(CH <sub>3</sub> ) <sub>3</sub> c	(сн <sub>3</sub> ) <sub>2</sub> снсн <sub>2</sub>	сн <sup>3</sup> ) <sup>3</sup> с	сн <sup>3</sup> ) <sup>3</sup> с	(CH <sub>3</sub> ) <sub>3</sub> C
35	T.	3 8	1	Yn 6-C1	Ħ	æ	6-C1.	6-c1	6-CÎ	6-01
40			·,	C-CF3	C-CF3	C-CF3	C-CF3	C-CF3	C-CF3	C-CF3
			,	m #	EO.	CH	8	H H	<del>E</del>	CH
45				O-C1	C-C1	СН	Н	C-C1	0 0	C-C1
50				Example Number 119	120	121	122	123	124	125

5		,	ပ ၀ ၈	63-65					
10		: :	R16 H	Ė	Ħ	н	, III	Ħ	н
15	a	·	R3 CH3CH2	cH <sub>3</sub> cH <sub>2</sub>	cH <sub>3</sub> cH <sub>2</sub>	CH <sub>3</sub> CH <sub>2</sub>	сн <sub>3</sub> (сн <sub>2</sub> ) <sub>2</sub> сн <sub>2</sub>	(сн <sub>3</sub> ) <sub>2</sub> сн	CH2CH2
25	TABLE III (Continued)	Y n NR3 R16	R (CH <sub>3</sub> ) <sub>3</sub> C	(CH <sub>3</sub> ) <sub>3</sub> C	$cH_3(cH_2)_5c(cH_3)_2$	<del>K</del>	(сн <sub>3</sub> ) <sub>3</sub> с	(CH <sub>3</sub> ) <sub>3</sub> C	сн <sup>3</sup> ) <sup>3</sup> с
30 35	TABI	H H H H H H H H H H H H H H H H H H H	Yn 6-Br	5,6-dicl	6-C1 CH	6-C1	6-01	6-01	6-c1
40			B W CH C-F	c-c1 c-c1	сн с-ст	CH C-CF3	CH C-CF3	CH C-CF3	CH C-CF3
45			A C-Br	c-c1	C-C1	c-cl	C-C1	c-c1	c-c1
50			Example Number 126	127	128	129	130	131	132

<b>5</b>					0 0 E	124-127	127-132		74-75			
10					81.6 7.1	H	ж	н	Ħ	Ħ	Ħ	Ħ
15 20			~		c o	(сн <sub>3</sub> ) <sub>2</sub> сн	сн <sub>3</sub> сн <sub>2</sub>	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> CH <sub>2</sub>	ch <sub>3</sub> ch <sub>2</sub>	ch <sub>3</sub> ch <sub>2</sub>	c <sub>6</sub> H <sub>5</sub> cH <sub>2</sub> cH <sub>2</sub>	CH2CH2
25			TABLE III (Continued)	NHN R R 6	<u>p</u>	•		с <sub>6</sub> н <sub>5</sub> с(сн <sub>3</sub> ) <sub>2</sub> с	×.	сн <sup>3</sup> ) <sup>3</sup> с		၂ ၂
30			TABLE II	7 d l B		pc1c <sub>6</sub> H <sub>5</sub>	pclc <sub>6</sub> H <sub>5</sub>	CeHS	$\triangle$	(CH <sub>3</sub>	(CH <sub>3</sub> ) <sub>3</sub> C	(сн <sub>3</sub> ) <sup>3</sup> с
35					. >-	6-C1	6-C1	6-C1	6-01	Ħ	Ħ	Ħ
40		•			: <b>:</b>	C-CJ	C-C1	C-CF3	C-CF3	Ж	C-CF3	C-CF3
	,				α	H H	CH	HO	H G	CH	H.	CH
45					d	C-C]	c-c1	C-C1	C-C1	C-CF3	c-c1	c-c1
50					Example Number	133	134	135	136	137	138	139

....

5			,	Do du					100.5-101.5
10				R: 16 H	Ħ	Ħ	н	н	щ
15 20	Ţ;	16		R <sub>3</sub>	cH <sub>3</sub> cH <sub>2</sub>	c <sub>6</sub> H <sub>5</sub> cH(cH <sub>3</sub> )	(CH <sub>3</sub> ) <sub>2</sub> NCH <sub>2</sub> CH <sub>2</sub>	$cH_3CH_2C(cH_3)_2$	N CH2CH2
<b>25</b> <b>30</b>	TABLE III (Continued	NR3R16	***	CH <sub>3</sub> ) <sub>3</sub> C	pclc <sub>6</sub> H <sub>5</sub> c(CH <sub>3</sub> ) <sub>2</sub>	сн <sup>3</sup> ) <sup>3</sup> с	сн <sup>3</sup> ) <sup>3</sup> с	(CH <sub>3</sub> ) <sub>3</sub> C	сн <sub>3</sub> ) 3 с
35	TAF	, m		Yn H	6-01	6-01	6-01	6-C1	6-61
40				B W C-CF <sub>3</sub>	CH C-CF3	CH C-CF3	CH C-CF3	CH C-CF3	CH C-CF3
45				A CH	C-C1	C-C1	C-C1	c-cl	C-CJ
50			1	Example Number 140	141	142	143	144	145

		•	1					
5			mp °C 202-202.5	,				
10			R16 H	Ħ	斑	Ħ	Ħ	Ħ
15 20	a	91	R3 CH <sub>3</sub> CH <sub>2</sub>	-CH2CH2	сн <sub>3</sub> сн <sub>2</sub>	сн <sub>3</sub> сн <sub>2</sub>	с <sub>6</sub> н <sub>5</sub> сн <sub>2</sub> сн <sub>2</sub>	с <sub>6</sub> н <sub>5</sub> сн <sub>2</sub>
25	TABLE III (Continued)	NR3 R16	(сн <sub>3</sub> ) <sub>3</sub> с	(CH <sub>3</sub> ) <sub>3</sub> c		کی پیری	сн <sub>3</sub> сн <sub>2</sub> с(сн <sub>3</sub> ) <sub>2</sub>	(сн <sup>3</sup> ) <sup>3</sup> с
30	TABLI	7 7 8	Yn 6-c1	6-Br	6-C1	6-C1	6-C1 (	6-01
40			B W C-CF 3	C-CF3	C-CF <sub>3</sub>	C-CF3	C-CF3	C-CF3
<b>4</b> 5			C-C1	C-Br CH	C-Cl CH	C-Cl CH	C-Cl CH	C-C1 CH
50			Example Number 146	147	148	149	150	151

\*Hydrochloride salt

	·	ပ							
5		O E			203-205		160-162		
10		EL6 CH3CH2	<b>#</b>	茁	#	ж	Ħ	ж	Ħ
15	<u>led).</u> 16	CH <sub>3</sub> CH <sub>2</sub>	сн3сн2	(сн <sub>3</sub> ) <sub>2</sub> сн	DCF30C6H5	neopentyl	H <sub>2</sub> NCOCCH(CH <sub>3</sub> ) <sub>2</sub>	N-CH2CH2	pclc <sub>e</sub> H <sub>5</sub> -cH <sub>2</sub> cH <sub>2</sub>
25	TABLE III (Continued)	(CH <sub>3</sub> ) <sub>3</sub> C	2.5 2.5	CI CI CH	clcH <sub>2</sub> c(cH <sub>3</sub> ) <sub>2</sub>	(сн <sub>3</sub> ) <sub>3</sub> с	(CH <sub>3</sub> ) <sub>3</sub> c	(CH <sub>3</sub> ) <sub>3</sub> C	(cH <sub>3</sub> ) <sub>3</sub> c
35	El Carlo	Yn 6-C1	6-01	6-01	6-C1	6-C1	6-c1	6-C1	6-01
40		B W C-CF <sub>3</sub>	1 C-CF3	1 C-CF3	1 C-CF3	1 C-CF3	1 C-CF3	1 C-CF3	I C-CF3
45		A B C-C1 CH	C-C1 CH	C-Cl CH	C-Cl CH	C-CI CH	c-cl ch	C-Cl CH	c-cl ch
50		Example Number 152	153	154	155	156	157	158	159

EP 0 604 798 A1

5	i.		၁၀ ဝဏ						
10			R16 H	Ħ	Ħ	æ	ж .	Ħ	Ħ
15 20	nued)	N <sub>3 16</sub> R	R3	CH <sub>2</sub> CH <sub>2</sub>	сн <sub>3</sub> (сн <sub>2</sub> ) <sub>4</sub> сн (сн <sub>3</sub> )	$(c_2H_5)_2^{N(CH_2)_3^{CH(CH_3)}}$	CH <sub>2</sub> =CHCH <sub>2</sub>	/l ch <sub>3</sub> ch <sub>2</sub>	CH <sub>3</sub> CH <sub>2</sub>
25 30	TABLE III (Continued)	NHN R	(CH <sub>3</sub> ) <sub>3</sub> C	(CH <sub>3</sub> ) <sub>3</sub> C	(CH <sub>3</sub> ) <sub>3</sub> C	) э <sup>ε</sup> ( <sup>ε</sup> нэ)	(CH <sub>3</sub> ) <sub>3</sub> C	1-methylcyclohexyl	сн <sub>3</sub> ) зс
35		_	Ул 6-С1	6-C1	6-C1	6-C1	6-c1	6-C1	5-CF3
40			C-CF <sub>3</sub>	C-CF3	C-CF3	C-CF3	C-CF3	C-CF3	HO .
			CH D	HU	HO	H H	Ж	H	СН
45	<i>:</i>		A C-C1	C-01	C-c1	C-C]	C-C1	c-c1	C-C1
50	÷ .		Example <u>Number</u> 160	161	162	163	164	165	166

5			O O E		
. 10			R16 H	ж	ж
15			R.3	2H <sub>2</sub>	N-CH <sub>2</sub> CH <sub>2</sub>
20	inued)	NR3 R1 6	CH <sub>3</sub> CH <sub>2</sub>	CH <sub>3</sub> CH <sub>2</sub>	
25	TABLE III (Continued	n huhu	(СН <sub>3</sub> ) <sub>3</sub> С	(сн <sub>3</sub> ) <sub>3</sub> с	(CH <sub>3</sub> ) <sub>3</sub> C
35	TAB		Yn 5,6-diF	6-Br	6-C1
40			B W C-F	CH C-F	сн с-сғ <sub>3</sub> 6-с1
<b>4</b> 5			C-F	C-Br	C-C1
50			Example Number 167	. 168	169

## **EXAMPLE 170**

Insecticidal and Acaricidal Evaluation of N-arylhydazine Derivatives

#### EP 0 604 798 A1

Test solutions are prepared by dissolving the test compound in a 35% acetone in water mixture to give a concentration of 10,000 ppm. Subsequent dilutions are made with water as needed.

# Spodoptera eridania, 3rd instar larvae, southern armyworm

A Sieva limabean leaf expanded to 7-8 cm in length is dipped in the test solution with agitation for 3 seconds and allowed to dry in a hood. The leaf is then placed in a 100 x 10 mm petri dish containing a damp filterpaper on the bottom and ten 3rd instar caterpillars. At 3 and 5 days, observations are made of mortality, reduced feeding, or any interference with normal molting.

#### Tetranychus urticae(OP-resistant strain), 2-spotted spider mite

Sieva limabean plants with primary leaves expanded to 7-8 cm are selected and cut back to one plant per pot. A small piece is cut from an infested leaf taken from the main colony and placed on each leaf of the test plants. This is done about 2 hours before treatment to allow the mites to move over to the test plant to lay eggs. The size of the cut, infested leaf is varied to obtain about 100 mites per leaf. At the time of test treatment, the piece of leaf used to transfer the mites is removed and discarded. The newly mite-infested plants are dipped in the test solution for 3 seconds with agitation and set in the hood to dry. After 2 days, one leaf is removed and mortality counts are made. After 5 days, another leaf is removed and observations are made of mortality of the eggs and/or newly emerged nymphs.

# <u>Diabrotic undecimpunctata howardi</u>, 3rd instar southern corn rootworm

One cc of fine talc is placed in a 30 ml wide-mouth screw-top glass jar. One mL of the appropriate acetone test solution is pipetted onto the talc so as to provide 1.25 mg of active ingredient per jar. The jars are set under a gentle air flow until the acetone is evaporated. The dried talc is loosened, 1 cc of millet seed is added to serve as food for the insects and 25 mL of moist soil is added to each jar. The jar is capped and the contents thoroughly mixed on a Vortex Mixer. Following this, ten 3rd instar rootworms are added to each jar and the jars are loosely capped to allow air exchange for the larvae. The treatments are held for 6 days when mortality counts are made. Missing larvae are presumed dead, since they decompose rapidly and can not be found. The concentrations used in this test correspond approximately to 50 kg/ha.

The tests are rated according to the scale shown below and the data obtained are shown in Tables IV, V and VI.

RATING SCALE							
Rate	Rate % Mortality		% Mortality				
0	no effect	5	56-65				
1	10-25	6	66-75				
2	26-35	7	76-85				
3	36-45	8	86-99				
4	46-55	9	100				

50

40

45

5

15

25

TABLE IV

Insecticidal and Acaricidal Evaluation
of N-Arylamidrazones

		% Mortality				
10	Compound (Ex. No.)	Armyworm <sup>1</sup> (300 ppm)	2-Spotted Mite <sup>2</sup> (300 ppm)	Corn Rootworm <sup>3</sup> (50 kg/ha)		
	85	0	0	100		
	86	100	0	80		
15	87	40	90	100		
	88					
20	89	o	.0	100		
	90	o	0	20		
	91	o	80	100		
25	92	o	. <b>0</b>	100		
	93	. 0	0	100		
30	94		80	100		
30	95	80	0	100		
	96	100	40	80		
35	97	o	0	100		
	98	40	0	40		
	100	0	40	0		
40	101	. 0	0	60		
	102	0	60	100		
45	103	40	0	100		
	104	. 0	90	50		
	105	20	0	90		
50	106	40	0	100		

# TABLE IV (Continued)

5		% Mortality				
40	Compound (Ex. No.)	Armyworm <sup>1</sup> (300 ppm)	2-Spotted Mite <sup>2</sup> (300 ppm)	Corn Rootworm <sup>3</sup> (50 kg/ha) 100		
10	107					
	108	90	50	100		
	109	0	0	50		
15	110	0	0	100		
	111	100	40	90		
20	112	40	100	20		
	113	20	100	100		
	114	40	100	100		
<b>25</b>	115	0	0	100		
	116	20	50	100		
30	117	20	0	100		
	118	50	70	100		
	119	100	50	90		
35	120		30	20		
	121	80	40	100		
40	122	0	0	40		
	123	o	0	60		
	124	50	80	100		
45	125	0	30	100		
	126	0	80	90		
50	128	0	0	30		
	129	100	40	<b>o</b>		

# TABLE IV (Continued)

Q.	Mo		. 7	• <b>+</b> •	
-16	mu	ILC	ユ⊥.	エレ)	1

		* MOI CATICY				
5	Compound (Ex. No.)	Armyworm <sup>1</sup> (300 ppm)	2-Spotted Mite <sup>2</sup> (300 ppm) 80	Corn Rootworm <sup>3</sup> (50 kg/ha)		
	130	80	80	100		
10	131	70	Ö	100		
	132		. 40	100		
45	133		0	0		
15	134	0	30	o		
	135	0	0	o		
20	136	0	70	100		
	137	0	0	100		
	138	0	0	100		
25	139	0	70	100		
	140	0	0	50		
30	141	100	o	0		
	142	0	0	100		
	143	0	0	100		
35	144	0	0	100		
	145	0	0	100		
40	146	0	0	100		
	147	0	0	100		
	148	50	0	100		
45	149	100	80	80 ·		
	150	0	60	100		
50	152	80	0	100		
		•				

## TABLE IV (Continued)

•	<b>%</b>	Mortalit
	•	TIOT COTTO

			* Mortality	
10	Compound (Ex. No.) 153	Armyworm <sup>1</sup> (300 ppm) 100	2-Spotted Mite <sup>2</sup> (300 ppm) 0	Corn Rootworm <sup>3</sup> (50 kg/ha) 100
	156		o	100
	157	0	o	100
15	158	40	o	100
	159	0	o	100
20	160	o	0	100
	161	0	0	***
	162	0	100	100
25	163	0	0	100
	164	O	0	100
30	167	0	0	100
	168	0	80	90
35	169	0	0	100

<sup>&</sup>lt;sup>1</sup>Armyworm is 3rd instar larvae, southern armyworm

50

45

40

<sup>&</sup>lt;sup>2</sup>2-Spotted Mite is 2-spotted spider mite (OP-resistant)

<sup>&</sup>lt;sup>3</sup>Corn Rootworm is 3rd instar southern corn rootworm

TABLE V

Insecticidal and Acaricidal Evaluation

# of N-Arylhydrazides

		<u> </u>	2,121	
	Compound (Ex. No.)	Armyworm <sup>1</sup> (300 ppm)	2-Spotted Mite <sup>2</sup> (300 ppm)	Corn Rootworm <sup>3</sup> (50 kg/ha)
10			,	
	1	8	0	9
	2	0	0	7
15	<b>3</b> .			9
	. 4	0	0	7
	5	Ò	0	8
20	. 6	o	0	0
	7	О	0	0
25	8	5	0	8
	9	O	0	0 .
	10	1	9	3
30	11	1	0	9
	12	4	0	4
or	13	О	9	3
35	14	7	0	7
	15	.9	0	3
40	16	О	0 .	0
	17	1	3	0
	18	2	0	6
45	19	9	0	0
	20	0 .	0	o
50	21	0	0	7
	22	o	0	0

# TABLE V(Continued)

5			% Mortality	
	Compound (Ex. No.)	Armyworm <sup>1</sup> (300 ppm) 0	2-Spotted Mite <sup>2</sup> (300 ppm) 0	Corn Rootworm <sup>3</sup> (50 kg/ha) 0
10	24	0	o	0
	25	9	0	8
	26	0	0	0
15	27	4	0	6
	28	2	0	0
20	29.	3	0	. 0
	30	0	2	4
	31	O	0	0
25	32	1	0	0
	33	o	0	. 0
30	34	8	0	2
	35	5	0	0
	36	8	0	0
35	- 37	4	0	0
	39	0	0	0
40	40	9	0	9
70	41	3	0	9
	42	0	2	. <b>4</b>

<sup>&</sup>lt;sup>1</sup>Armyworm is 3rd instar larvae, southern armyworm

55

. 45

<sup>&</sup>lt;sup>2</sup>2-Spotted Mite is 2-spotted spider mite (OP-resistant)

 $<sup>^{3}</sup>$ Corn Rootworm is 3rd instar southern corn rootworm

#### **TABLE VI**

	Insecticidal and Acaricidal Evaluation of Substituted N-Arylhydrazinoyl Halides					
5	Compound (Ex. No.)	,				
		Armyworm <sup>1</sup> (300 ppm)	2-Spotted Mite <sup>2</sup> (300 ppm)	Corn Rootworm <sup>3</sup> (50 kg/ha)		
	78	90	90	0		
	54	80	100	0		
10	58	• 0	0 .	0		
	59	0	100	0		
	64		90	100		
	66	; <b>80</b>	100	20		
	. 71	90	90	30		
15	73	50	100	0		
	· <b>7</b> 7	100	90	80		
	79	100	100	· 100		

<sup>&</sup>lt;sup>1</sup>Armyworm is 3rd instar larvae, southern armyworm

### **Claims**

20

25

30

35

50

55

 A method for the control of insect or acarid pests which comprises contacting said pests or their food supply, habitat or breeding grounds with a pesticidally effective amount of a compound having the structure

**(I)** 

wherein

A is C-R<sub>4</sub> or N;
B is C-R<sub>5</sub> or N;
W is C-R<sub>6</sub> or N with the proviso that at least one of A, B or W must be other than N;
Y is halogen, CN, NO<sub>2</sub>, C<sub>1</sub>-C<sub>6</sub>alkyl, C<sub>1</sub>-C<sub>6</sub>haloalkyl, C<sub>1</sub>-C<sub>6</sub>alkoxy or C<sub>1</sub>-C<sub>6</sub>haloalkoxy;
n is an integer of O, 1 or 2;
Q is

 $N = \langle {}^{NR_3R_{16}}_{R}, N = \langle {}^{X_1}_{R}, {}^{R_2}_{N} \rangle \langle {}^{R_3}_{R}, {}^{R_1}_{R} \rangle \langle {}^{R_1}_{R}, {}^{R_2}_{R} \rangle \langle {}^{R_1}_{R}, {}^{R_2}_{R}, {}^{R_2}_{R} \rangle \langle {}^{R_1}_{R}, {}^{R_2}_{R}, {}^{R_2}_{R},$ 

R is hydrogen,

<sup>&</sup>lt;sup>2</sup>2-Spotted Mite is 2-spotted spider mite (OP-resistant)

<sup>&</sup>lt;sup>3</sup>Corn Rootworm is 3rd instar southern corn rootworm

 $C_1\text{-}C_1\text{-}\text{0}$  alkyl optionally substituted with one or more halogens,  $C_3\text{-}C_6$  cycloalkyl,  $C_1\text{-}C_4$  alkoxy,  $C_1\text{-}C_4$  haloalkoxy,  $(C_1\text{-}C_4$  alkyl)SO\_x,  $(C_1\text{-}C_4$  haloalkyl)SO\_x, phenyl optionally substituted with one to three halogen,  $C_1\text{-}C_4$  alkyl,  $C_1\text{-}C_4$  haloalkyl,  $C_1\text{-}C_4$  alkoxy,  $C_1\text{-}C_4$  haloalkyl)SO\_x,  $(C_1\text{-}C_4$  haloalkyl)SO\_x,  $(C_1\text{-}C_4$  haloalkyl)SO\_x,  $(C_1\text{-}C_4\text{-}\text{haloalkyl})$ SO\_x,  $(C_1\text{-}C$ 

phenoxy optionally substituted with one to three halogen,  $C_1$ - $C_4$  alkyl,  $C_1$ - $C_4$  haloalkyl,  $C_1$ - $C_4$  alkoxy,  $C_1$ - $C_4$  haloalkoxy,  $(C_1$ - $C_4$  alkyl)SO<sub>x</sub>,  $(C_1$ - $C_4$  haloalkyl)SO<sub>x</sub>,  $(C_1$ - $(C_4$  ha

 $C_3$ - $C_{1\,2}$  cycloalkyl optionally substituted with one or more halogens,  $C_1$ - $C_6$  alkyl,  $C_1$ - $C_6$  haloalkyl,  $C_1$ - $C_4$  alkoxy,  $C_1$ - $C_4$  haloalkoxy,  $(C_1$ - $C_4$  haloalkyl)> $SO_x$ ,  $(C_1$ - $C_4$  haloalkyl)> $SO_x$ ,

phenyl optionally substituted with one to three halogen, C<sub>1</sub>-C<sub>4</sub>alkyl, C<sub>1</sub>-C<sub>4</sub> haloalkyl, C<sub>1</sub>-C<sub>4</sub> alkoxy, C<sub>1</sub>-C<sub>4</sub> haloalkoxy,NO<sub>2</sub> or CN groups, or phenoxy optionally substituted with one to three halogen, C<sub>1</sub>-C<sub>4</sub>alkyl, C<sub>1</sub>-C<sub>4</sub> haloalkyl, C<sub>1</sub>-C<sub>4</sub>alkoxy, C<sub>1</sub>-C<sub>4</sub> haloalkoxy,NO<sub>2</sub> or CN groups, or phenyl optionally substituted with one or more halogen, C<sub>1</sub>-C<sub>4</sub>alkyl, C<sub>1</sub>-C<sub>4</sub> haloalkyl, C<sub>1</sub>-C<sub>4</sub> alkoxy, C<sub>1</sub>-C<sub>4</sub> haloalkoxy, NO<sub>2</sub> or CN groups;

are each independently hydrogen or C<sub>1</sub>-C<sub>4</sub> alkyl;

are each independently hydrogen,

 $C_1$ - $C_{10}$ alkyl optionally substituted with one or more halogen, hydroxy,  $C_1$ - $C_4$ alkoxy,  $(C_1$ - $C_4$ alkyl)SO<sub>x</sub>, CONR<sub>7</sub>R<sub>8</sub>, CO<sub>2</sub>R<sub>9</sub>, R<sub>10</sub>, R<sub>11</sub>,

 $C_3\text{-}C_6\text{-}\text{cycloalkyl}$  optionally substituted with one to three halogen,  $C_1\text{-}C_4\text{-}\text{alkyl},\ C_1\text{-}C_4\text{-}\text{haloalkyl},\ C_1\text{-}C_4\text{-}\text{alkoxy},\ C_1\text{-}C_4\text{-}\text{haloalkoxy},\ NO_2$  or CN groups,

phenyl optionally substituted with one or more halogen, C<sub>1</sub>-C<sub>4</sub> alkyl, C<sub>1</sub>-C<sub>4</sub> haloalkyl, C<sub>1</sub>-C<sub>4</sub> alkoxy, C<sub>1</sub>-C<sub>4</sub> haloalkoxy,CO<sub>2</sub> or CN groups, or pyridyl optionally substituted with one or more halogen, C<sub>1</sub>-C<sub>4</sub> alkyl, C<sub>1</sub>-C<sub>4</sub> haloalkyl, C<sub>1</sub>-C<sub>4</sub> alkoxy, C<sub>1</sub>-C<sub>4</sub> haloalkoxy,NO<sub>2</sub> or CN groups,

 $C_3$ - $C_{10}$  alkenyl optionally substituted with one or more halogen, hydroxy,  $C_1$ - $C_4$  alkoxy,  $(C_1$ - $C_4$  alkyl)SO<sub>x</sub>, CONR<sub>7</sub>R<sub>8</sub>, CO<sub>2</sub>R<sub>9</sub>, R<sub>10</sub>, R<sub>11</sub>,

 $C_3\text{-}C_6$  cycloalkyl optionally substituted with one to three halogen,  $C_1\text{-}C_4$  alkyl,  $C_1\text{-}C_4$  haloalkyl,  $C_1\text{-}C_4$  alkoxy,  $C_1\text{-}C_4$  haloalkoxy,  $NO_2$  or CN groups,

phenyl optionally substituted with one or more halogen,  $C_1$ - $C_4$  alkyl,  $C_1$ - $C_4$  haloalkyl,  $C_1$ - $C_4$  alkoxy,  $C_1$ - $C_4$  haloalkoxy,  $CO_2$  or CN groups, or

pyridyl optionally substituted with one or more halogen,  $C_1$ - $C_4$ alkyl,  $C_1$ - $C_4$ haloalkyl,  $C_1$ - $C_4$ alkoxy,  $C_1$ - $C_4$ haloalkoxy, $NO_2$  or CN groups,

 $C_3$ - $C_{10}$  alkynyl optionally substituted with one or more halogen, hydroxy,  $C_1$ - $C_4$  alkoxy,  $(C_1$ - $C_4$  alkyl)SO<sub>x</sub>, CONR<sub>7</sub>R<sub>8</sub>, CO<sub>2</sub>R<sub>9</sub>, R<sub>10</sub>, R<sub>11</sub>,

 $C_3\text{-}C_6$  cycloalkyl optionally substituted with one to three halogen,  $C_1\text{-}C_4$  alkyl,  $C_1\text{-}C_4$  haloalkyl,  $C_1\text{-}C_4$  alkoxy,  $C_1\text{-}C_4$  haloalkoxy,  $NO_2$  or CN groups,

phenyl optionally substituted with one or more halogen, C<sub>1</sub>-C<sub>4</sub>alkyl, C<sub>1</sub>-C<sub>4</sub>haloalkyl, C<sub>1</sub>-C<sub>4</sub>alkoxy, C<sub>1</sub>-C<sub>4</sub>haloalkoxy,CO<sub>2</sub> or CN groups, or

pyridyl optionally substituted with one or more halogen, C<sub>1</sub>-C<sub>4</sub>alkyl, C<sub>1</sub>-C<sub>4</sub>haloalkyl, C<sub>1</sub>-C<sub>4</sub>alkoxy, C<sub>1</sub>-C<sub>4</sub>haloalkoxy,NO<sub>2</sub> or CN groups,

C<sub>3</sub>-C<sub>12</sub>cycloalkyl optionally substituted with one or more halogen, hydroxy, C<sub>1</sub>-C<sub>4</sub> alkoxy, (C<sub>1</sub>-C<sub>4</sub> alkoyl)SO<sub>x</sub>, CONR<sub>7</sub>R<sub>8</sub>, CO<sub>2</sub>R<sub>9</sub>, R<sub>10</sub>, R<sub>11</sub>,

 $C_3$ - $C_6$  cycloalkyl optionally substituted with one to three halogen,  $C_1$ - $C_4$  alkyl,  $C_1$ - $C_4$  haloalkyl,  $C_1$ - $C_4$  alkoxy,  $C_1$ - $C_4$  haloalkoxy,  $NO_2$  or CN groups

phenyl optionally substituted with one or more halogen, C<sub>1</sub>-C<sub>4</sub>alkyl, C<sub>1</sub>-C<sub>4</sub>haloalkyl, C<sub>1</sub>-C<sub>4</sub>alkoxy, C<sub>1</sub>-C<sub>4</sub>haloalkoxy,CO<sub>2</sub> or CN groups, or pyridyl optionally substituted with one or more halogen, C<sub>1</sub>-C<sub>4</sub>alkyl, C<sub>1</sub>-C<sub>4</sub>haloalkyl, C<sub>1</sub>-C<sub>4</sub>alkoxy, C<sub>1</sub>-C<sub>4</sub>haloalkoxy,NO<sub>2</sub> or CN groups or may be taken together to form a ring represented by the structure

 $R_1$  and  $R_2$   $R_3$  and  $R_{16}$ 

25

5

10

15

20

30

35

40

45

50

55

R<sub>3</sub> and R<sub>15</sub>

R<sub>4</sub>, R<sub>5</sub> and R<sub>6</sub>

are each independently hydrogen, halogen, CN, NO2, (C1-C4 alkyl)- $SO_x$ , $(C_1-C_4$ haloalkyl) $SO_x$ ,  $C_1-C_6$ alkyl,  $G_1-C_6$ haloalkyl,  $C_1-C_6$ alkoxy or  $C_1-C_6$ 

C<sub>6</sub> haloalkoxy;

R<sub>7</sub>, R<sub>8</sub> and R<sub>9</sub>

are each independently hydrogen or C1-C4 alkyl;

 $R_{10}$ 

is NR<sub>12</sub>R<sub>13</sub>,

15

10 🙏

5

$$X_r$$
 or  $CH_2$ 

20

R<sub>11</sub>

25

30

35

are each independently hydrogen or C1-C4 alkyl;  $R_{12}$ ,  $R_{13}$ ,  $R_{14}$  and  $R_{15}$ 

Х is O, S or NR<sub>14</sub>;

 $X_1$ is chlorine, bromine or fluorine;

is

is an integer of 0 or 1;

p and m

are each independently an integer of 0, 1, 2 or 3 with the proviso that only

one of p, m or r can be 0 and with the further proviso that the sum of p +

m + r must be 4, 5 or 6;

is an integer of 0, 1 or 2; or the acid addition salts thereof with the proviso that when Q is

40

$$N = < X_1$$

45

R is  $C_1$ - $C_5$  alkyl and  $X_1$  is chlorine, then either at least one of A, B or W must be N or  $R_4$ ,  $R_5$ ,  $R_6$  and Y must be other than hydrogen and n must be O and with the further proviso that when Q is

50

55

$$\stackrel{\mathsf{N}}{=}\stackrel{\mathsf{X}_1}{\stackrel{\mathsf{R}}{=}}$$

- The method according to claim 1 wherein

R is phenyl or substituted phenyl and X<sub>1</sub> is chlorine, then at least one of A, B or W must be N.

5

The method according to claim 2 wherein A is C-R4, B is CH, W is C-R6, Y is halogen, n is 1, R1 is hydrogen, R4 and R6 are each independently halogen or C1-C6 alkyl substituted with one or more halogens, and R, R<sub>3</sub> and R<sub>15</sub> are each independently hydrogen or C<sub>1</sub>-C<sub>10</sub>alkyl.

10

The method according to claim 1 wherein Q is

A compound having the structure

15

20

The method according to claim 4 wherein R<sub>1</sub> and R<sub>2</sub> are hydrogen, R is C<sub>1</sub>-C<sub>6</sub> alkyl, A is C-R<sub>3</sub>, B is C-R<sub>4</sub>, W is C-R<sub>5</sub>, Y is halogen, n is 1, R<sub>3</sub> is halogen, R<sub>4</sub> is hydrogen and R<sub>5</sub> is C<sub>1</sub>-C<sub>6</sub> alkyl substituted with one or more halogens.

6. 25

The method according to claim 5 wherein the compound is 2,2-dimethylpropionic acid, 2-(2,6-dichloro- $\alpha,\alpha,\alpha$ -trifluoro-p-tolyl)hydrazide.

30

35

wherein A, B, W, Y, n, R, R<sub>1</sub>, R<sub>3</sub> and R<sub>16</sub> are described in claim 1 with the proviso that when all of A, B and W are other than N, then R and one of R<sub>3</sub> or R<sub>16</sub> are other than hydrogen and with the further proviso that when one of A, B or W is N, then Y, R4, R5 or R6 must be other than C1-C10alkyl.

40

The compound according to claim 7 having the structure

45

50

55

wherein

R

is C1-C10alkyl;

is hydrogen or C<sub>1</sub>-C<sub>4</sub>alkyl;

 $R_1$ Rз

is C<sub>1</sub>-C<sub>10</sub>alkyl;

is hydrogen or C<sub>1</sub>-C<sub>10</sub>alkyl; and

R<sub>4</sub>, R<sub>6</sub> and Y

are each independently hydrogen, halogen, CN, NO2, C1-C6 alkyl, C1-C6 haloalkyl,

C<sub>1</sub>-C<sub>6</sub> alkoxy or C<sub>1</sub>-C<sub>6</sub> haloalkoxy.

- 9. The compound according to claim 8 N-ethyl-2,2- dimethylpropionamide, 2-(2,6-dichloro-α,α,α-trifluoro-p-tolyl)hydrazone
- 10. A process for the preparation of a compound having the stucture

wherein A, B, W, Y, n, R,  $R_1$ ,  $R_3$  and  $R_{16}$  are described in claim 1 which comprises reacting a compound having the structure

with at least one molar equivalent of an amine compound, HNR<sub>3</sub>R<sub>16</sub>.

11. A composition for controlling insect or acarid pests which comprises an inert liquid or solid carrier and a pesticidally effective amount of a compound of formula I

(I)

wherein A, B, W, Y, n, R<sub>1</sub> and Q are described in claim 1.

12. The composition according to claim 11 wherein the formula I compound has the structure

$$R_{6} \xrightarrow{Y} R_{1} N = NR_{3}R_{16}$$

$$R_{4}$$

and

10

15

20

25

30

35

40

45

50

55

R is  $C_1$ - $C_{10}$  alkyl;

 $R_1$  is hydrogen or  $C_1$ - $C_4$  alkyl;

EP 0 604 798 A1 is C<sub>1</sub>-C<sub>10</sub>alkyl; Rз  $R_{16}$ is hydrogen or C<sub>1</sub>-C<sub>10</sub>alkyl; and are each independently hydrogen, halogen, CN, NO2, C1-C6 alkyl, C1-C6 haloalkyl,  $R_{\!\scriptscriptstyle 4}\,,\,R_{\!\scriptscriptstyle 6}$  and Y $C_1$ - $C_6$  alkoxy or  $C_1$ - $C_6$  haloalkoxy. 5 10 15 20 25

50

30

35

40

45

: 55

ategory	Citation of document with it of relevant pa	dication, where appropriate,	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.CL5)
(	GB-A-736 473 (BATAA * claim 1 *	FSCHE PETROLEUM)	1-3,11,	A01N37/28 A01N37/52 A01N43/40
(	EP-A-0 325 983 (HOE * claims *	CHST)	1,4,11	A01N43/58 C07C257/22
	US-A-3 745 215 (G. * column 1, line 30		1,11	
	US-A-3 917 849 (R. * claims *	BOESCH)	1,11	·
	US-A-3 935 315 (R. * claims *	BOESCH)	1,11	
,P	DE-A-42 00 591 (BAY * claims *	ER)	1,11	
	FR-A-2 105 698 (ROU * claims 1,3,4 *	SSEL-UCLAF)	7,10,11	TECHNICAL FIELDS SEARCHED (Int.Cl.5)
	US-A-3 214 334 (H.E * column 1, line 11		11	AO1N CO7C
	FR-A-2 184 974 (BAY * claims *	ER)	11	
	US-A-3 879 542 (G. * claims *	KAUGARS)	1	
	US-A-3 505 403 (H.G * claim 6 *	. VIEHE)	7,8	
		-/		
	The present search report has b	een drawn up for all claims		
	Place of search	Date of completion of the search	_	Exemples
	THE HAGUE	15 April 1994	Dec	corte, D
X : par Y : par doc	CATEGORY OF CITED DOCUME ticularly relevant if taken alone ticularly relevant if combined with an nument of the same category theological background	E : earlier pate after the fi  other D : document L : document	cited in the application cited for other reasons	lished on, or n

EPO FORM 1500 02.82 (POACOL)

Category	Citation of document with i	indication, where appropriate,	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.CL5)
x	JOURNAL OF ORGANIC vol. 38, no. 7, 19 pages 1344 - 1348 R.F.SMITH ET AL. 'A *compounds 5,16*	CHEMISTRY 073 , EASTON US	7,8,10	
X	TRANSACTIONS 2 1986 pages 537 - 541	AL. 'Acid, base, and sation of z- to e-	7,8,10	·
	no. 1 , 1971 , PARI pages 283 - 286	ETE CHIMIQUE DE FRANCE S FR 'Recherches sur les	7,8	
X	CHEMICAL ABSTRACTS, 26 May 1980, Columb abstract no. 180607 * abstract * & ZH. ORG. KHIM. vol. 15, no. 11 , 1 pages 2280 - 2287	ous, Ohio, US; 'j,	7,8	TECHNICAL FIELDS SEARCHED (Int.Cl.5)
	The present search report has b	een drawn up for all claims		N
	Place of search	Date of completion of the search		Exceptiner
	THE HAGUE	15 April 1994	Dec	orte, D
X : part Y : part doc: A : tech O : non	CATEGORY OF CITED DOCUME icularly relevant if taken alone icularly relevant if combined with an ument of the same category inological background -written disclosure rmediate document	E : earlier patent d after the filing Other D : document cited L : document cited	ocument, but publi date I in the application for other reasons	ished on, or

EPO PORM 1503 03.12 (POICU)